Elucidation of the Reversible Carbon Monoxide Reactions of a Paramagnetic Rhodium(II) Complex

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Coordination of carbon monoxide to the rhodium(II) ether–phosphine complex [Rh(tmpp)$_2$][BF$_4$]$_2$ **1** [tmpp = tris(2,4,6-trimethoxyphenyl)phosphine] initiates a redox reaction to produce the rhodium(III) complex [Rh(tmpp)$_2$][BF$_4$]$_3$ **2** and the dicarbonyl rhodium(I) species [Rh(tmpp)$_2$(CO)$_2$][BF$_4$] **3**; the latter readily loses a CO ligand to form [Rh(tmpp)$_2$(CO)][BF$_4$] **4** which enters into a second redox reaction with **4** to regenerate the original rhodium(II) radical **1**.

We have been developing routes to stable rhodium(II) complexes for small molecule binding studies.[1] Such reactions are of considerable interest as a comparison with the rich chemistry exhibited by cobalt(II) complexes.[2] Several years ago we synthesized and structurally characterized the paramagnetic ether–phosphine complex [Rh(tmpp)$_2$][BF$_4$]$_2$ [tmpp = tris(2,4,6-trimethoxyphenyl)phosphine] which exhibits unusual stability in the solid state and in solution. This molecule has a unique coordination environment for rhodium which consists of two phosphorus atoms in a *cis*-arrangement and four oxygen interactions from pendant methoxy groups. To our knowledge, this molecule represents the first fully characterized mononuclear rhodium(II) species,[3] and, as such, it provides a unique opportunity to investigate the chemistry of rhodium(II) with an unpaired electron. We are studying small molecule reactions of [Rh(tmpp)$_2$]$^{2+}$ and herein report our preliminary findings on the CO binding of this complex.

Within minutes, treatment of a purple CH$_2$Cl$_2$ solution of [Rh(tmpp)$_2$][BF$_4$]$_2$ **1** with CO at room temperature and 1 atm produced an orange-red solution which exhibits ν(C≡O) at 2011 cm^{-1}. No further IR spectral changes were noted even after several hours under a CO atmosphere.† A parallel ^{1}H NMR study in CD$_2$Cl$_2$ indicated the formation of two diamagnetic species. Rapid purging of the reaction solution with Ar or N$_2$ rapidly converted the carbonyl compound with ν(C≡O) 2011 cm^{-1} to a new product with ν(C≡O) at 1970 cm^{-1}, which itself disappeared within 10 minutes to produce a solution of the original Rh^{II} compound as judged by its characteristic EPR, optical and redox properties. This

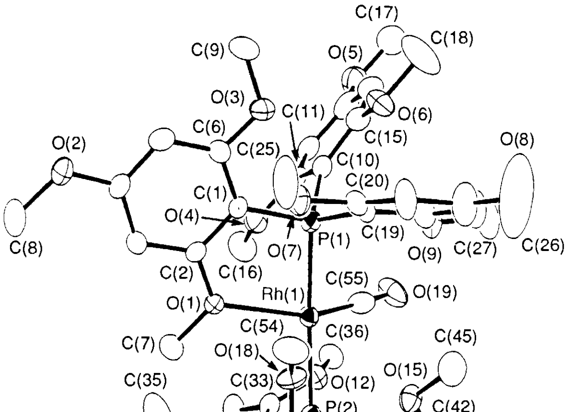

Fig. 1 ORTEP drawing of the [Rh(tmpp)$_2$CO]$^+$ **4** cation with unique atom labelling scheme. Selected bond distances (Å) and angles (°) are: Rh(1)–P(1), 2.316(3); Rh(1)–P(2), 2.354(3); Rh(1)–O(1), 2.319(7); Rh(1)–C(55), 1.78(1); Rh(1)–O(18), 2.611(7); P(1)–Rh(1)–P(2), 175.0(1); P(1)–Rh(1)–O(1), 78.1(2); P(1)–Rh(1)–C(55), 91.3(3); P(2)–Rh(1)–O(1), 103.2(2); P(2)–Rh(1)–C(55), 89.8(3); O(1)–Rh(1)–C(55), 150.2(4).

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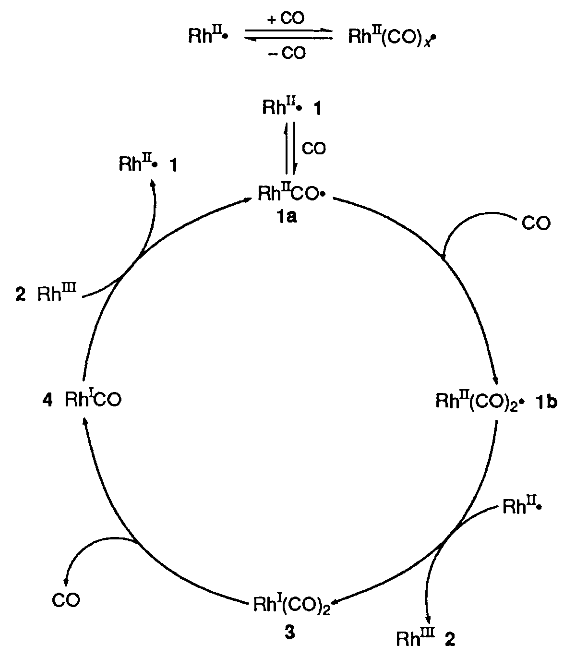
† In several experiments at high concentrations, an IR band at ν(C≡O) 1725 cm^{-1} was observed. This species is under further investigation.

fascinating transformation constitutes a reversible CO binding reaction which we have unravelled by a preliminary study of the structure, redox properties and reactivity of key stable intermediates.

Addition of diethyl ether to the orange-red reaction solution under a CO atmosphere precipitated a red solid **2** from a yellow filtrate. Concentration of the yellow solution yielded a pale yellow crystalline compound **4** [ν(C≡O): CH_2Cl_2, 1970 cm^{-1}; Nujol mull, 1958 cm^{-1}]. In solution and in the solid state, product **4** readily uptakes an additional equivalent of CO to give a bright yellow compound **3** with ν(C≡O) at 2011 cm^{-1}. The ^1H NMR, redox and IR properties of **2** are identical to those previously observed for the Rh^{III} complex $[Rh(tmpp)_2][BF_4]_3$ which we have independently synthesized by a deliberate oxidation of $[Rh(tmpp)_2]^{2+}$.‡ This Rh^{III} complex is one of the two products observed during the *in situ* ^1H NMR study (*vide supra*). A full report on the properties and X-ray structure of this molecule will be published elsewhere.[4]

X-Ray quality crystals of **4** were grown by slow diffusion of a benzene layer into a solution of the compound in CH_2Cl_2.§ An ORTEP drawing of **4**, shown in Fig. 1, reveals the identity of the product as a mono-carbonyl complex of Rh^I. One phosphine ligand acts as a bidentate group *via* a weak pendant ether interaction in addition to the Rh–P bond, while the second tmpp group binds only through the P atom. Note that an isomerization of the phosphine groups from *cis* to *trans* has occurred in going from **1** to **4** (*vide supra*). The coordination sphere is completed by a CO ligand to give an overall highly distorted square-planar geometry; the magnitude of the distortion is evidenced by the angle C(55)–Rh(1)–O(1) of 150.2(4)°. The Rh–ether interaction, Rh(1)–O(1), = 2.319(7) Å. It can be seen from Fig. 1 that in fact three other methoxy oxygens are oriented towards the Rh atom and one of them is just outside the sum of the covalent bonding radii: Rh(1)–O(18) 2.611(7), Rh(1)–O(15) 3.122(8), and Rh(1)–O(4) 3.177(8) Å. It appears, then, that the molecule, whose structure is between square-planar and trigonal bipyramidal, has at least one protecting group, O(18), positioned on the open side of the molecule. In contrast to the solid-state structure, the solution form of **4** exhibits equivalent tmpp ligands as evidenced by ^1H and ^{31}P NMR studies.‡ The dynamic process which exchanges all potentially interacting *ortho*-methoxy groups continues to −90 °C, thus demonstrating the extreme lability of the ether interactions. A similar exchange process was noted in the complex $[(\eta^3\text{-tmpp})Mo(CO)_3]$.[5]



Scheme 1 Proposed scheme for reversible reaction of CO with Rh^{II}•**1** {Rh^{II} • ≡ $[Rh(tmpp)_2][BF_4]_2$}

Complex **3**, produced by addition of CO to **4**, was crystallized from a CO-saturated solution of CH_2Cl_2–Et_2O, and its crystal structure determined.§ This molecule exhibits strict square-planarity as expected for a *trans* Rh^I complex of general formula $Rh(CO)_2(PR_3)_2$. The IR and NMR properties of **3** confirmed its identity as the carbonyl species observed in the aforementioned IR monitoring studies.‡

From the above data, we conclude the following. The Rh^I and Rh^{III} compounds **3** and **2** are produced by a rapid electron transfer following CO binding to the Rh^{II} centre. Provided a CO atmosphere is maintained, these are the sole products of the reaction. Upon purging with an inert gas, a molecule of CO is lost from **3** to give **4**, whose redox properties [$E_{1/2}$(ox) + 0.50 V] indicate an accessible oxidation to Rh^{II}(CO) effected by the Rh^{III} complex **2** [$E_{1/2}(\text{red})_1$ +0.46] which itself is reduced back to Rh^{II} **1**. This redox chemistry has been confirmed by a deliberate 1:1 reaction between isolated samples of **2** and **4**. The unstable Rh^{II}(CO) species can easily lose CO or cycle back into the redox reaction. Eventually, however, all species in solution are converted back to Rh^{II}. An outline of this mechanism is presented in Scheme 1 with the short-lived adducts **1a** and **1b** as postulated requisite intermediates. The reason for invoking a dicarbonyl $Rh^{II}(CO)_2$ adduct follows from the known redox properties of **2**–**4**. That is, a mono-carbonyl species Rh^{II}(CO) **1a** cannot be responsible for the initial electron-transfer reaction with Rh^{II} **1** to give **2** and **4** since the reverse redox reaction between Rh^I(CO) **4** and Rh^{III} **2** is known to occur. Attempts to observe **1a** and **1b** by fast IR and EPR techniques are in progress.

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‡ $[Rh(tmpp)_2][BF_4]_3$ **2**: ^1H NMR (δ in CD_2Cl_2): 2.93, 3.57, 3.59, 3.64, 3.90, 3.92, 3.97, 4.19, 4.69 (s, OMe), 5.73, 6.05, 6.18, 6.32, 6.50, 6.88 (dd, *meta*); $^{31}P\{^1H\}$ NMR (δ in CD_2Cl_2 rel. to 85% H_3PO_4) 37.4 (d, $J_{Rh\text{-}P}$ 107 Hz); cyclic voltammetry (*E*/V *vs.* Ag/AgCl in mol dm^{-3} $Bu^n{}_4NBF_4$ in CH_2Cl_2): $E_{1/2}$ $(\text{red})_1$ +0.46, $E_{1/2}$ $(\text{red})_2$ −0.65.

$[Rh(tmpp)_2(CO)][BF_4]$ **4**: ^1H NMR (δ in CD_2Cl_2]: 3.48 (s, *o*-OMe), 3.80 (s, *p*-OMe), 6.04 (t, $^4J_{P\text{-}H}$ 2.1 Hz, *meta*); $^{31}P\{^1H\}$ NMR (δ in CD_2Cl_2 rel. to 85% H_3PO_4): −11.1 (d, $J_{Rh\text{-}P}$ 128 Hz); CV (as for **2**): $E_{1/2}$(ox) +0.50 V. (Found: C, 50.6; H, 5.0. $C_{55}H_{66}F_4P_2O_{19}BRh$ requires C, 51.5; H, 5.2%).

$[Rh(tmpp)_2(CO)_2][BF_4]$ **3** ^1H NMR (δ in CD_2Cl_2): 3.41 (s, *o*-OMe), 3.79 (s, *p*-OMe), 6.02 (t, $^4J_{P\text{-}H}$ 2.1 Hz); $^{31}P\{^1H\}$ NMR (δ in CD_2Cl_2 relative to 85% H_3PO_4): −23.8 (d, $J_{Rh\text{-}P}$ 116 Hz); CV (as for **2**): $E_{p,a}$ = +0.80 V.

§ *Crystal data* for **4**: $RhP_2C_{67}O_{19}BF_4H_{78}$, $M = 1439.01$, triclinic, space group $P\bar{1}$, $a = 14.898(5)$, $b = 18.060(8)$, $c = 14.343(4)$ Å, $\alpha = 96.56(4)$, $\beta = 113.84(2)$, $\gamma = 104.80(4)°$, $U = 3308(2)$ Å^3, $Z = 2$, $D_c = 1.438$ g cm^{-1}, $F(000) = 1496$, μ(Cu-Kα) = 32.60 cm^{-1}. Data were collected on a Rigaku AFC5R diffractometer at 23 ± 1 °C by using the ω–2θ scan technique ($2\theta_{max}$ 120.3°). The data were corrected for Lorentz and polarization effects. In addition, an empirical absorption correction was applied based on azimuthal scans of several reflections with χ near 90°. Of the 9855 unique data collected, 6393 data with $I > 3.00\sigma(I)$ were used in refinement. Refinement of 757 parameters converged with residuals of $R = 0.067$ and $R_w = 0.069$.

Crystal data for **3**: $RhCl_2P_2C_{57}O_{20}BF_4H_{88}$ (not illustrated), M = 1395.73, triclinic, space group $P\bar{1}$, $a = 13.318(4)$, $b = 13.404(2)$, $c = 18.164(4)$ Å, $\alpha = 95.908(3)$, $\beta = 97.037(3)$, $\gamma = 90.711(3)°$, $U = 3200(2)$ Å^3, $Z = 2$, $D_c = 1.448$ g cm^{-3}, $F(000) = 1440$, μ(Mo-Kα) = 4.71 cm^{-1}. Data were collected on a Nicolet P3/F diffractometer at −96 °C by using the ω-scan method with 2θ in the range $4 \leqslant 2\theta \leqslant 45°$. The data were corrrected for Lorentz and polarization effects. Of the 8801 unique data collected, 5934 data with $I > 3.00\sigma(I)$ were used in refinement. Refinement of 779 parameters resulted in residuals of $R = 0.059$, $R_w = 0.084$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

It is interesting to note in the context of this work that Wayland and coworkers have recently demonstrated the coupling of CO ligands and the activation of methane by using bulky-ligand-stabilized Rh^{II} centres.[6] We are investigating the possibility of tailoring our phosphine ligand to favour similar chemistry.

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